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(54) Foam control agents based on organopolysiloxanes

Schaumkontrollmittel auf Basis von Polyorganosiloxanen

Agents anti-mousse à base de polyorganosiloxanes

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(56) References cited:
US-A- 4 690 713

- **DATABASE WPI Derwent Publications Ltd., London, GB; AN 85-179878 & JP-A-60 106 507 (SHINETSU CHEM IND KK) 12 June 1985**
- **PATENT ABSTRACTS OF JAPAN vol. 14, no. 480 (C-0771) 19 October 1990 & JP-A-02 198 603 (SHIN ETSU CHEM CO LTD) 7 August 1990**
- **PATENT ABSTRACTS OF JAPAN vol. 15, no. 373 (C-0869) 19 September 1991 & JP-A-03 151 004 (DOW CORNING KK) 27 June 1991**
- **DATABASE WPI Week 8002, Derwent Publications Ltd., London, GB; AN 80-02397C & JP-A-54 149 388 (TOSHIBA SILICONE KK)**

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Description

[0001] The present invention relates to foam control agents. More specifically the present invention relates to foam control agents which are based on organopolysiloxanes having higher alkyl groups substituted on some of the silicon atoms.

[0002] Foam control agents which are based on organopolysiloxanes have been known for a long time, and have found applications in a large number of industries, e.g. detergent industry, textile industry and paper industry. A large number of organopolysiloxane based foam control agents use polydimethylsiloxanes which are end-blocked by trimethylsilyl groups. Much research has gone into improving such foam control agents with varying measures of success. There is a continuing need to find more effective and robust foam control agents.

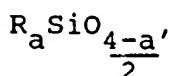
[0003] Certain types of hydrocarbonsilicone copolymers have been suggested in U.S. specification 4,514,319 for the improvement of the antifoaming ability of compositions based on hydrocarbon oils as the antifoam vehicle, particularly mineral oil. In said specification there is disclosed a hydrocarbon oil based silicone antifoam composition which comprises from 1 to 60 weight percent of a hydrocarbonsilicone copolymer, from 1 to 20 weight percent of a hydrophobic filler having a certain average particle size, from 20 to 97 weight percent of a hydrocarbon carrier oil and optionally an organosilicone surfactant and a silicone oil. The hydrocarbonsilicone copolymer may be a random copolymer or a block copolymer, but has to fulfil the condition that the %CH₂ content is in the range of about 30% to about 70%. This condition has to be fulfilled in order to ensure that the hydrocarbonsilicone is soluble in the hydrocarbon carrier oil and that there is sufficient surface activity at the oil/air interface to decrease the surface tension at low concentrations, and thus spread on a surfactant solution, e.g. on 0.5% aqueous solution of sodium dodecyl sulphate. This CH₂% is not clearly defined in the specification, but from the examples can be read as meaning the number percentage of CH₂ groups which are present in the larger hydrocarbon substituents based on the total number of carbon atoms present in the copolymer. Hydrocarbonsilicone copolymers with a %CH₂ which is lower than 30% or higher than 70% have been disclosed, but do not improve the performance of the hydrocarbon oil based anti-antifoam. There is no indication that similar hydrocarbon-silicone copolymers could be useful as foam control agent without the presence of a hydrocarbon oil.

[0004] JP-A-60106507 describes a powdered antifoam containing an antifoaming component with at least one of an organopolysiloxane of the formula (R¹)_a (CH₃)_b SiO_{4-a-b/2} where R¹ is a hydrocarbon radical of one to 1 to 20 carbon atoms; a polyether containing organopolysiloxane and a polyalkyleneglycol. The specific examples describe dimethylpolysiloxane as the only organopolysiloxane used alone.

[0005] US4690713 describes an antifoam composition which may contain an organopolysiloxane fluid with a viscosity in the range of 20 to 1,000,000 centistokes at 25°C and having organic side chains comprising from 1 to 20 carbon atoms. The only examples provided of such organopolysiloxane fluids related to the use of polydimethylsiloxane fluid. A different type of siloxane has been suggested in E.P. Specification 397 297 for use in combination with hydrocarbon oils and finely divided filler particles. The siloxane materials are alkylaminosilicones wherein at least one silicon atom is substituted with an amino containing group which has a C₆₋₅₀ hydrocarbon radical linked directly to a nitrogen atom. These materials are stated only to be useful if similar conditions are fulfilled to those required of the hydrocarbon silicon copolymers of U.S. Specification 4,514,319. This means that the alkylamino-silicones have to be soluble in hydrocarbon oils and still possess excellent surface activity. These conditions are stated to be fulfilled if the alkylaminosilicones have a methylene content of at least 1% by weight, preferably 5 to 10%, and if they exert a surface tension lowering on the hydrocarbon oils of at least 0.005 Nm⁻¹ (5 dynes/cm). The test applied in said patent specification if the CH₂ content (calculated as number of methylene groups over the sum of methylene groups and methyl groups x 100) is from 45 to 90%, most preferably from 50 to 75%, and if the resulting mixture of the silicone with mineral oil spreads over a 0.5% by weight solution of sodium dodecylsulphate in water.

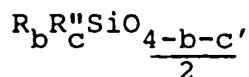
[0006] We have now found that foam control agents can be improved by leaving out hydrocarbon oils and using as the organopolysiloxane an organopolysiloxane which has a certain amount of higher alkyl groups linked directly or indirectly to silicon atoms. This is surprising, as these organopolysiloxane materials do not spread on an aqueous solution of 0.5% by weight sodium dodecylsulphate and are therefore traditionally regarded as unsuitable for anti-foaming purposes.

[0007] According to a first aspect of the invention there is provided a foam control agent, which is free from hydrocarbon oils, and comprises (A) from 70 to 99.9 parts by weight of an organopolysiloxane of which the siloxane units consist essentially for 0 to 60% of units of the general formula (I)



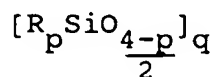
wherein R denotes a hydrocarbon group having up to 8 carbon atoms and a has a value of from 0 to 3, and for 40 to

100% of units of the general formula (ii)

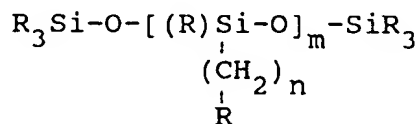


wherein R'' denotes a group -Z_z-R', wherein R' denotes an alkyl group having from 9 to 35 carbon atoms, Z denotes a linking group between silicon and R' and z has a value of 0 or 1, b has a value of 0, 1 or 2, c has a value of 1 or 2, and b+c has a value of 1, 2 or 3, provided more than 70% by weight of the carbon content of the organopolysiloxane is due to the groups R'', (B) from 0.1 to 30 parts by weight of a finely divided hydrophobic particulate material and (C) from 0 to 20 parts by weight of an organo-silicon resin consisting essentially of triorganosiloxane groups and SiO_{4/2} groups.

[0008] Some organopolysiloxanes which are useful in the present invention are known materials and have been described in a number of publications. For example U.S. specification 3,756,052 describes a metal working lubricant in which an organopolysiloxane is used which has the formula



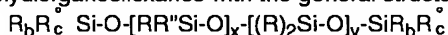
in which R is selected from monovalent hydrocarbon or halohydrocarbon groups having from 1 to 19 carbon atoms, at least 30% of the R substituents being alkyl radicals containing from 8 to 18 carbon atoms. In U.S. specification 5,017,221 there is described an emulsion which is useful as a protective coating for surfaces such as rubber, which comprises polymethylalkylsiloxane having the general formula



wherein R is methyl, m is an integer from 1 to 3000 and n is an integer from 1 to 10.

[0009] Polydiorganosiloxanes (A) which are useful in the composition of the present invention have at least units of the formula (ii), although they may also have some units of formula (i). Preferred organopolysiloxanes are those where from 40 to 100% of all units are units of formula (ii), more preferably 60 to 100%. It is also preferred that the value of a in formula (i) and the value of b+c in formula (ii) is 2 for the majority of units, making the organopolysiloxane (A) predominantly a polydiorganosiloxane with a linear structure.

[0010] In the preferred organopolysiloxanes the linear polymer is end-capped with units wherein a or b+c has a value of 3. It is, however, also possible that one of the substituents of the terminal silicon atoms in the preferred organopolysiloxanes is a hydroxyl group or an alkoxy group, having 1 to 6 carbon atoms. Thus preferred organopolysiloxanes are polydiorganosiloxanes with the general structure



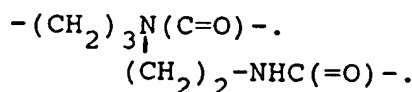
wherein R and R'' are as defined above, R^o denotes either a group R or a group R'', b and c are as defined above and x and y each independently denote an integer. The values of x and y are not crucial in these preferred organopolysiloxanes. They may range from 0 to many hundreds, giving polymers with a viscosity which may be very low or very high, even up to many thousands of mm²/s. It is required, however, that the molecule fulfils the conditions set out above with regard to the number of units having a group R''. Preferred however are those polymers where the total chain length (x+y+2) includes from about 40 to about 500 units, most preferably 60 to 400 units.

[0011] It is also required that the organopolysiloxanes have a carbon content where more than 70% by weight is due to presence of groups R''. More preferably the carbon content attributed to the groups R'' is at least 75%, most preferably from 80 to 90% by weight. This can be achieved by several means. It is possible to use R' groups which are long chain alkyl groups. Alternatively, or in conjunction, it is possible to allow a high proportion of units of formula (ii) in the siloxane polymer.

[0012] Preferred R' groups are those which have a carbon chain of from 10 to 24, more preferably 10 to 18. Examples of suitable groups R' are dodecyl, tetradecyl, octadecyl and eicosyl. The groups R denote hydrocarbon groups with up to 8 carbon atoms. These may be for example alkyl, aryl, alkenyl, alkylaryl, arylalkyl or alkynyl groups. Preferably at least 50% of all R groups are alkyl groups, more preferably at least 80%. It is particularly preferred that the R groups are methyl or ethyl groups, most preferably methyl.

[0013] Polyorganosiloxanes (A) may be prepared by any of the known methods. For example they may be formed

by hydrolysing silanes which have two hydrolysable groups and one group R and one group R' as silicon-bonded substituents. Alternatively they may be provided by reacting organopolysiloxanes which have a number of reactive groups substituted on silicon atoms with certain organic groups having higher alkyl groups. Depending on the type of group which is present on the silicon atoms, and the type of alkyl containing group with which they are reacted, the group Z may vary, and may even not be present at all. For example if an organopolysiloxane has silicon bonded hydrogen atoms which are reacted with α,β -alkenes having from 9 to 35 carbon atoms, having its olefinic unsaturation between the first 2 carbon atoms in the presence of a catalyst which promotes the addition reaction between Si-H and the unsaturation, resulting in the group R'' being equal to the group R' (z=0). Suitable catalysts for this reaction include platinum and rhodium based complexes. Suitable alkenes include 1,2-dodecene, 1,2-octadecene and 1,2-eicosene. Although this method is preferred, resulting in each R'' group being a group R', there are many other ways of linking higher alkyl groups to a siloxane polymer. These methods are well known in the art and include condensation of a silanol group with an alcoholic group, a silicon-bonded hydrogen atom with an alcoholic group or a silanol group with an ether, all resulting in Z being an oxygen link. Other reactions include silanol groups or alkoxy substituted silicon atoms with carboxylic acids or epoxides, amino functional siloxanes with epoxy functional organic groups or lactones and alkenyl functional silicone with a mercapto group. The resulting group Z may therefore be one of a number of divalent linking groups, consisting of O or C, H and optionally O, N, S or P atoms or C, H, O and optionally N, S or P atoms. Oxygen, when present, would be in the form of an ether oxygen, an ester oxygen or a substituted hydroxyl or alkoxy group. Nitrogen, when present, would be in the form of amino groups or, if present, with oxygen in the form of an amido group. Suitable examples of Z groups include alkylene ester groups, alkylene ether groups, amide groups, polyamino/amido groups and mercapto groups, for example -O-, -CH₂CH₂O-C(=O)-, -CH₂CH₂O-CH₂-CH(OH)-, -(CH₂)₃NHC(=O)-, -(CH₂)₃NH-CH₂-C(=O)-, -CH₂CH₂S- and



[0014] Component (B) is a finely divided hydrophobic particulate material. Suitable particulate materials are well-known in the art of foam control and include e.g. silica, titania, alumina, ground quartz, magnesium oxide, zinc oxide, salts of aliphatic carboxylic acids, e.g. calcium or aluminium stearates, reaction products of isocyanates with certain materials, for example cyclohexylamine and alkyl amides, e.g. ethylene or methylene bis stearamide. Preferred are silica particles, especially those having an average particle size of from 0.1 to 50 μ , preferably from 1 to 20 μ and a surface area of at least 50 m²/g. These silica particles can be rendered hydrophobic e.g. by treating them with dialkylsilyl groups and/or trialkylsilyl groups either bonded directly onto the silica or by means of a silicone resin. We prefer to employ a silica the particles of which have been rendered hydrophobic with dimethyl and/or trimethyl silyl groups. Suitable silica materials include fumed silica, precipitated silica, hydrothermal silica and gel formation silica. Preferably the amount of particulate material used in the foam control agent is from 1 to 20 parts by weight, more preferably 3 to 15 parts, most preferably 5 to 8 parts. A foam control agent according to the invention may contain a mixture of different particulate materials.

[0015] Component (C) is an optional ingredient in the foam control agent according to the invention. It consists essentially, and preferably only, of monofunctional groups of the formula R₃SiO_{1/2} and tetrafunctional groups SiO_{4/2}, although minor amounts of difunctional or trifunctional siloxane groups may also be present. A small number of the silicon-bonded substituents may also be hydroxyl or alkoxy groups, but this should not exceed 3% of all silicon-bonded substituents. R is as defined above but it is preferred that the group R is a lower alkyl (i.e. C₁₋₃) group, most preferably methyl. The ratio of monofunctional to tetra-functional units is preferably in the range of from 1/4 to 4/1, most preferably 1/2 to 2/1. The presence of this ingredient tends to improve the efficiency of the foam control agent. It is accordingly preferred that Component (C) is present in an amount of from 3 to 15 parts, most preferably 5 to 10 parts by weight.

[0016] Additional optional components for the foam control agent are thickeners, e.g. polyvinyl alcohols, Al stearates, monoglycerides, triglycerides, treated silicas, petroleum jelly, paraffin waxes, microcrystalline waxes, dispersing agents, levelling agents, wetting agents, inorganic salts, viscosity regulators, preservatives, rust inhibitors, antioxidants and pH modifiers. Although the foam control agents are preferably used as the only such agent present they may also be used in combination with other foam control agents, e.g. stearate soaps.

[0017] The foam control agent may be made by simply mixing the ingredients in any order and ensuring good dispersion. Where the finely divided particulate material is already hydrophobic no further reaction is required. Where this is not the case, making the particulate material hydrophobic may be done in situ, e.g. by heating the mixture where the hydrophobing agent is added. Where an unwanted byproduct is generated, e.g. water or ammonia, as the result of e.g. condensation reactions between the agent and the particulate material these byproducts are preferably removed, e.g.

by heating under reduced pressure.

[0018] A foam control agent according to the invention may be used in its pure form, in emulsified form or in a dispersed form, e.g. a self-dispersible form. The emulsion is particularly useful where the foam control agent has to be stored in an aqueous system, e.g. a liquid detergent composition. Emulsification may be done according to standard and well known methods.

[0019] Foam control compositions according to the present invention are useful in a number of different applications where foam is generated in an aqueous system. Examples are liquors of paper manufacturing systems, textile dying baths, food processing systems, cutting oils and detergent washing liquors. Foam control agents according to the present invention have been found particularly efficient with powder detergent compositions. Where traditional silicone-based foam control agents require special treatment to maintain their efficiency when stored with powder detergent compositions such as encapsulation in waxes, fatty acids or similar higher melting materials, it has been unexpectedly found that foam control agents according to the present invention retain their efficiency much better than prior art compositions when not protected by such means as encapsulation. This is particularly true for those organopolysiloxanes which have a degree of polymerisation of from 60 to 200 and where 70 to 100% of all silicon atoms have a R" group substituent. Most useful are organopolysiloxanes wherein the degree of polymerisation is 80 to 120 and the amount of silicon atoms which have an R" group is from 75 to 90%. A particularly useful organopolysiloxane has a degree of polymerisation of 80 and 80% of all silicon atoms with a R" group.

[0020] The present invention also provides in another of its aspects a detergent composition in powder form, comprising a detergent component and a foam control agent according to the invention. The foam control agent control composition according to the invention may be added to the detergent component in a proportion of from 0.02 to 25% by weight based on the total detergent composition. Preferably foam control agents are added in a proportion of from 0.05 to 5% by weight based on the total detergent composition.

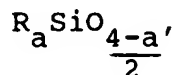
[0021] Suitable detergent components comprise an active detergent, organic and inorganic builder salts and other additives and diluents. The active detergent may comprise organic detergent surfactants of the anionic, cationic, non-ionic or amphoteric type or mixtures thereof. Suitable anionic organic detergent surfactants include alkali metal soaps of higher fatty acids, alkyl aryl sulphonates, for example sodium dodecyl benzene sulphonate, long chain (fatty) alcohol sulphates, olefine sulphates and sulphonates, sulphated monoglycerides, sulphated ethers, sulphosuccinates, alkane sulphonates, phosphate esters, alkyl isothionates, sucrose esters and fluorosurfactants. Suitable cationic organic detergent surfactants include alkylamine salts, quaternary ammonium salts, sulphonium salts and phosphonium salts. Suitable non-ionic organic surfactants include condensates of ethylene oxide with a long chain (fatty) alcohol or fatty acid, for example C₁₄₋₁₅ alcohol, condensed with 7 moles of ethylene oxide (Dobanol 45-7), condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxides, fatty acid alkylol amides and fatty amine oxides. Suitable amphoteric organic detergent surfactants include imidazoline compounds, alkylamino-acid salts and betaines. Examples of inorganic components are phosphates and polyphosphates, silicates, such as sodium silicates, carbonates, sulphates, oxygen releasing compounds, such as sodium perborate and other bleaching agents and zeolites. Examples of organic components are anti-redeposition agents such as carboxy methyl cellulose (CMC), brighteners, chelating agents, such as ethylene diamine tetra-acetic acid (EDTA) and nitrilotriacetic acid (NTA), enzymes and bacteriostats. Materials suitable for the detergent component are well known to the person skilled in the art and are described in many text books, for example Synthetic Detergents, A. Davidsohn and B.M. Milwidsky, 6th edition, George Godwin (1978).

[0022] Foam control compositions according to the present invention may be mixed in with the other ingredients of the detergent composition in any suitable way. For example they may be mixed in mechanically or sprayed onto the powdered detergent composition.

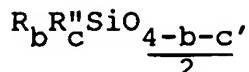
[0023] The foam control agents according to the present invention are particularly useful in systems where there is a high degree of turbulence during operation of an aqueous surfactant solution, i.e. in environments with free surface turbulence. With the expression 'environment with free surface turbulence' is meant an environment in which an aqueous surfactant solution undergoes agitation, be it mechanically or otherwise, which causes mixing of gas and liquid at the liquid/gas interface and entrainment of the one phase into the other. In one embodiment this agitation forces at least some of the liquid of the surfactant solution above the gas/liquid interface. This liquid then falls back onto the surface of the liquid, which may cause foam to be generated. In an alternative embodiment liquid is introduced from above the interfacial surface into the bulk. Examples of environments which are subject to free surface turbulence are front loading washing machines, jet dying systems which are not fully submerged, fountains and high speed sparging. Examples of environments where free surface turbulence does not take place include low speed sparging, top loading washing machines with a simple and slow agitation system and slow speed mixing systems, especially where higher viscosity liquids are mixed.

[0024] The invention provides, according to yet another aspect, a method of controlling the foam of an aqueous surfactant solution in an environment with free surface turbulence which comprises mixing said solution with 5×10^{-4} to 10% by weight of the surfactant solution of a foam control agent, comprising (A) from 70 to 99.9 parts by weight of a

polydiorganosiloxane which consists essentially of 0 to 60% units of the general formula



wherein R denotes a hydrocarbon group having up to 8 carbon atoms and \underline{a} has a value of from 0 to 3, and 40 to 100% units of the general formula (ii)



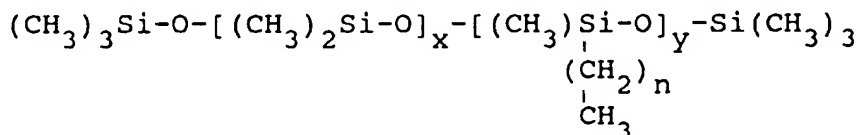
wherein R'' denotes an alkyl group having from 9 to 35 carbon atoms, \underline{b} has a value of 0, 1 or 2, \underline{c} has a value of 1 or 2, and $\underline{b+c}$ has a value of 1, 2 or 3, provided more than 70% by weight of the carbon content of the organopolysiloxane is due to the groups R'', (B) from 0.1 to 30 parts by weight of a finely divided hydrophobic particulate material and (C) from 0 to 10 parts by weight of an organo-silicon resin consisting essentially of triorganosiloxane groups and $SiO_{4/2}$ groups.

[0025] The foam control agent may be mixed by addition to a surfactant composition, e.g. detergent composition, prior to this being placed in the aqueous solution, or by mixing the appropriate amount of foam control agent into the aqueous solution.

[0026] There now follow a number of examples in which all parts and percentages are by weight unless otherwise indicated.

Preparation of Foam Control Agents

[0027] Organopolysiloxanes (A) were prepared by hydrosilylation reaction of the corresponding hydrosiloxane with the corresponding alkene in the presence of a Pt catalyst. They have the general formula



wherein the values for \underline{x} , \underline{y} and \underline{n} are as shown in Table I.

TABLE I

Polyorganosiloxane	x	y	n
1	0	59	9
2	0	59	11
3	0	59	13
4	12	48	13
5	12	48	17
6	32	48	13
7	32	48	15
8	32	48	17
9	60	40	13
10	60	40	15

TABLE I (continued)

Polyorganosiloxane	x	y	n
11	60	40	17
12	60	40	19-23
13	60	40	23
14	80	48	14

[0028] Foam control agents were prepared by mixing the above organopolysiloxanes with a particulate material which was selected from (A) a precipitated silica treated with polydimethylsiloxane supplied by Degussa GmbH, (B) a fumed silica treated with dimethyl silane, also supplied by Degussa GmbH, (C) a gel-formation silica supplied by W.R. Grace Company treated in situ with trimethylsilyl groups, (D) a fumed silica treated with hexamethyldisilazane supplied by Cabot Corporation, (E) a fumed silica treated with dimethylsilane, also supplied by Cabot Corporation, (F) an untreated fumed silica supplied by Cabot Corporation, treated in situ with trimethylsilyl groups, (G) a fumed silica treated with trimethylsilane supplied by Wacker GmbH, (H) ethylene bis-stearyl-amide, (I) a hydrothermal silica supplied by Degussa GmbH, treated in situ with dimethylpolysiloxane and (J) a precipitated silica supplied by Degussa GmbH, treated in situ with dimethylpolysiloxane. In some cases an MQ resin (K) was also added. Foam Control agents AF1 to AF14 comprised 95 parts of organopolysiloxanes 1 to 14 respectively and 5 parts of Filler A. Table II shows the other foam control agents which were prepared. In brackets is given the amount of particulate material used in % by weight based on combined siloxane and particulate material weight.

TABLE II

Foam Control Agent	Polyorganosiloxane	Particulate Material
AF15	11	D (2.7)
AF16	11	D (5.4)
AF17	11	E (2.7)
AF18	11	G (2.7)
AF19	11	B (2.7)
AF20	11	F (2.7)
AF21	11	F (5.4)
AF22	11	C (5.0)
AF23	11	H (8.0)
AF24	11	A (5.0) + K (5.0)
AF25	11	A (5.0) + K (10.0)
AF26	15	A (5.0) + K (5.0)
AF27	1	A (5.0) + K (5.0)
AF28	2	A (5.0) + K (5.0)
AF29	3	A (5.0) + K (5.0)
AF30	4	A (5.0) + K (5.0)
AF31	6	A (5.0) + K (5.0)
AF32	11	I (5.0)
AF33	14	I (5.0)
AF34	11	J (5.0)

[0029] Two comparative foam control agents were prepared. CAF1 was a prior art foam control agent according to

the teaching of E.P. application 501, comprising a branched polydimethyl siloxane polymer and 5% by weight of a hydrophobic silica particulate material. CAF2 comprises a silicone polymer which has a chain length of 400 siloxane units, of which 30 have a octadecyl substituent, and 5% by weight of a hydrophobic silica. CAF3 comprises a silicone polymer which has a chain length of 100 siloxane units, of which 25 have a octadecyl substituent, and 5% by weight of a hydrophobic silica. CAF2 and CAF3 are outside the scope of the invention as respectively only 40% and 70% of their carbon content is due to the higher alkyl groups.

Testing of the Foam Control Agents in Detergent Compositions

[0030] Foam control efficiency was tested in a front loading washing machine (Miele® 427) using a 3.5kg load of clean cotton pillow cases, and a washing cycle of 40°C or of 95°C. As detergent composition was used about 70g of a composition free from foam control agents of any description. They were selected from (DET1) a formulation based on alkyl benzyl sulphonate, alkyl polyethylene oxide, sodium tripolyphosphate and sodium perborate, (DET2) or (DET3) formulations supplied by a commercial detergent manufacturer based on anionic surfactants, including sodium dodecyl benzene sulphonate, nonionic surfactants including alkyl ethoxylate, perborate bleach, bleach activators, enzymes, zeolites and sequestering agents or (DET4) another formulation supplied by a commercial detergent manufacturer, based on linear anionic surfactants, including sulphonates and sulphates, nonionic surfactants, perborate bleach, bleach activators, enzymes, zeolites and sequestering agents. DET2 and DET4 are substantially more foaming than DET1 and DET3. The foam control efficiency was related to the amount of foam generated during the washing cycle and is expressed by the amount of foam control required (as a percentage by weight of the detergent composition) to keep the foam level below the 100% mark of the window of the machine, when the drum is stationary. The results are given in Table III.

TABLE III

	Foam Control	Detergent	Washing	Required
	Agent	Composition	Cycle	Level
5	AF 1	DET1	40	0.12
	AF 1	DET1	95	0.10
10	AF 1	DET3	40	0.12
	AF 1	DET3	95	0.10
	AF 3	DET2	40	0.20
15	AF 3	DET2	95	0.09
	AF 3	DET3	95	0.09
	AF 4	DET1	40	0.18
	AF 4	DET1	95	0.04
20	AF 4	DET2	95	0.10
	AF 4	DET3	40	0.08
	AF 4	DET3	95	0.10
25	AF 5	DET1	40	0.18
	AF 6	DET1	40	0.18
	AF 6	DET1	95	0.035
30	AF 6	DET2	95	0.10
	AF 6	DET3	95	0.09
	AF 7	DET1	40	0.23
	AF 8	DET1	40	0.15
35	AF 8	DET1	95	0.037
	AF 8	DET2	95	0.08
	AF 8	DET3	95	0.08
40	AF 9	DET1	40	0.40
	AF 9	DET1	95	0.10
	AF10	DET1	40	0.25

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TABLE III (cont)

	Foam Control	Detergent	Washing	Required
	Agent	Composition	Cycle	Level
5	AF11	DET1	40	0.13
	AF11	DET1	95	0.041
10	AF11	DET2	95	0.13
	AF11	DET3	95	0.11
	AF12	DET1	40	>1.0
15	AF13	DET1	40	>1.0
	AF14	DET1	40	0.18
	AF14	DET1	95	0.035
	AF15	DET1	40	0.20
20	AF15	DET1	95	0.06
	AF16	DET1	40	>0.3
	AF16	DET1	95	0.06
25	AF17	DET1	95	0.095
	AF18	DET1	40	0.20
	AF18	DET1	95	0.10
30	AF19	DET1	40	>0.2
	AF20	DET1	40	>0.3
	AF21	DET1	40	>0.3
35	AF21	DET1	95	0.095
	AF22	DET1	40	0.13
	AF22	DET1	95	0.050
	AF23	DET1	40	0.184
40	AF23	DET1	95	0.08
	AF24	DET1	40	0.12
	AF24	DET1	95	0.03
45	AF25	DET1	40	0.12
	AF25	DET1	95	0.03
	AF26	DET1	40	0.13
50	AF26	DET1	95	0.03
	AF27	DET2	95	0.10

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TABLE III (cont)

	Foam Control	Detergent	Washing	Required
	Agent	Composition	Cycle	Level
5	AF27	DET4	95	0.40
	AF28	DET4	95	0.50
10	AF29	DET4	95	0.50
	AF30	DET4	95	0.50
	AF31	DET4	95	0.40
15	AF31	DET4	95	0.40
	AF32	DET1	95	0.04
	AF33	DET1	95	0.04
	AF34	DET1	40	0.06
20	CAF1	DET1	40	0.40
	CAF2	DET1	40	0.80
	CAF3	DET1	40	>1.0
25	CAF3	DET3	95	>0.5

[0031] From Table III it is clear that the foam control agents according to the invention perform better than those materials outside the invention. AF12 and AF13 did not perform well at a 40°C wash because the melting point of the organopolysiloxanes is higher than the washing temperature. In higher temperature applications, however, performance will be better.

Storage Stability

[0032] Foam control tests were carried out, as explained above, for detergent compositions which were stored at 40°C for 2 or 4 weeks. The foam control agent was added to the detergent composition without any encapsulant. Test results given in Table IV show the percentage of loss in performance after storage, compared to the initial test without storage, calculated as the percentage increase required to achieve the same level of foam control.

TABLE IV

Foam Control Agent	Detergent Composition	Storage 2 Weeks	Storage 4 Weeks
AF 4	DET2	0	10
AF 6	DET2	0	20
AF 8	DET2	20	20
AF11	DET2	40	50
AF 4	DET3	0	0
AF 6	DET3	10	20
AF 8	DET3	20	20
AF11	DET3	20	30
CAF1	DET2	200	-

[0033] It is clear from the results that storage stability of the foam control agents is better for detergent compositions, where the foam control agent is merely added to the powder of the detergent composition, than it is for prior art foam control agents.

5 Testing of Foam Control Agents in Cutting Oils

[0034] One litre of a cutting oil composition was prepared by mixing 5% of a commercially available cutting oil concentrate, Alusol® B from Castrol Corp, with soft water. The composition was placed in a 2 litre beaker which was equipped with a pumping system. The pumping system drew the composition from the beaker through a stainless steel tube and allowed the composition to drop back onto the surface of the composition within the beaker from a height of 15cm. Before the circulation started a certain amount of foam control agent was added and the circulation was continued for 3 hours. If at the end of the three hours the foam level was less or more than 300ml on the top of the surface of the composition, the test was repeated with amended concentrations of foam control agent, until the level after three hours had reached 300ml exactly. The concentration of foam control agent required to reach that condition is reported in Table V below. The foam control agents used were AF3 and AF29 as defined above. Two comparative foam control agents were also tested. These were commercially available foam control agents Discocheck® from Exxon Corp. and Tensipar® from ICI Plc.

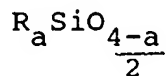
TABLE V

Foam Control Agent	Concentration required to achieve 300ml foam at the end of 3 hours
Discocheck	0.20%
Tensipar	0.19%
AF3	0.14%
AF29	0.05%

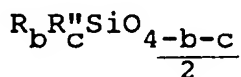
[0035] It is clear that considerable improvement was achieved by using compositions according to the invention.

Claims

1. A foam control agent which is free from hydrocarbon oils and comprises an organopolysiloxane (A), a finely divided hydrophobic particulate matter (B) and optionally an organosilicon resin (C), characterised in that it comprises from 70 to 99.9 parts by weight of organopolysiloxane (A) of which the siloxane units consist essentially for 0 to 60% of units of the general formula (i)

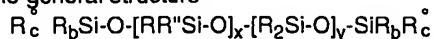


wherein R denotes a hydrocarbon group having up to 8 carbon atoms and \underline{a} has a value of from 0 to 3, and for 40 to 100% of units of the general formula (ii)



wherein R" denotes a group -Z-R' wherein R' denotes an alkyl group having from 9 to 35 carbon atoms, Z denotes a linking group between silicon and R' and \underline{a} has a value of 0 or 1, b has a value of 0, 1 or 2, \underline{c} has a value of 1 or 2 and $\underline{b+c}$ has a value of 1, 2 or 3, provided more than 70% by weight of the carbon content of the organopolysiloxane is due to the groups R", from 0.1 to 30 parts by weight of a finely divided hydrophobic particulate material (B) and from 0 to 20 parts by weight of an organosilicon resin (C) consisting essentially of triorganosiloxane groups and SiO_{4/2} groups.

2. A foam control agent according to Claim 1 characterised in that the organopolysiloxanes are polydiorganosiloxanes with the general structure



wherein R and R'' are as defined above, R^o denotes either a group R or a group R'', b and c are as defined above, and x and y each independently denote an integer.

3. A foam control agent according to Claim 2 characterised in that the total chain length (x+y+2) includes from 40 to 500 siloxane units.

4. A foam control agent according to any one of the preceding claims characterised in that the R' groups have a carbon chain of from 10 to 24 atoms.

5. A foam control agent according to any one of the preceding claims characterised in that Component (B) is silica having an average particle size of from 0.1 to 50µ and a surface of at least 50m²/g, said surface having been rendered hydrophobic.

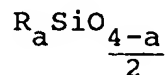
6. A foam control agent according to any one of the preceding claims characterised in that Component (C) is present in an amount of from 5 to 10 parts by weight.

7. A foam control agent according to any one of the preceding claims characterised in that it is provided in the form of an emulsion or a dispersion.

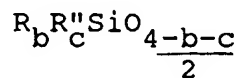
8. A detergent composition in powder form comprising a detergent component and a foam control agent, characterised in that the foam control agent is according to any one of the preceding claims.

9. A detergent composition according to Claim 8 characterised in that the foam control agent is present in an amount of from 0.02 to 25% by weight based on the total detergent composition.

10. A method of controlling the foam of an aqueous surfactant solution in an environment with free surface turbulence which comprises mixing said solution with 5 x 10⁻⁴ to 10% by weight of the surfactant solution of a foam control agent characterised in that the foam control agent comprises (A) from 70 to 99.9 parts by weight of an organopolysiloxane of which the siloxane units consist essentially for 0 to 60% of units of the general formula (i)



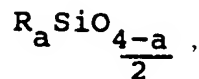
wherein R denotes a hydrocarbon group having up to 8 carbon atoms and a has a value of from 0 to 3, and for 40 to 100% of units of the general formula (ii)



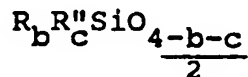
wherein R'' denotes a group -Z_z-R' wherein R' denotes an alkyl group having from 9 to 35 carbon atoms, Z denotes a linking group between silicon and R' and z has a value of 0 or 1, b has a value of 0, 1 or 2, c has a value of 1 or 2 and b+c has a value of 1, 2 or 3, provided more than 70% by weight of the carbon content of the organopolysiloxane is due to the groups R'', (B) from 0.1 to 30 parts by weight of a finely divided hydrophobic particulate material and (C) from 0 to 20 parts by weight of an organosilicon resin consisting essentially of triorganosiloxane groups and SiO_{4/2} groups.

Patentansprüche

1. Schaumsteuerungsmittel, das keine Kohlenwasserstofföle enthält und ein Organopolysiloxan (A), ein feinteiliges hydrophobes teilchenförmiges Material (B) und optional ein Organosiliciumharz (C) umfaßt und dadurch gekennzeichnet ist, daß es 70-99,9 Gew.-Teile eines Organopolysiloxans (A), dessen Siloxaneinheiten im wesentlichen aus 0-60% Einheiten der allgemeinen Formel (i)



worin R für eine Kohlenwasserstoffgruppe mit bis zu 8 Kohlenstoffatomen steht und a einen Wert von 0 bis 3 besitzt, und aus 40-100% Einheiten der allgemeinen Formel (ii)



bestehen, worin R'' für eine Gruppe -Z-R' steht, worin R' für eine Alkylgruppe mit 9 bis 35 Kohlenstoffatomen steht, Z für eine Verbindungsgruppe zwischen Silicium und R' steht und z einen Wert von 0 oder 1 besitzt, b einen Wert von 0, 1 oder 2 besitzt, c einen Wert von 1 oder 2 besitzt und b+c einen Wert von 1, 2 oder 3 besitzt, wobei gilt, daß mehr als 70 Gew.-% des Kohlenstoffgehalts des Organopolysiloxans auf die Gruppen R'' zurückzuführen ist,

0,1 bis 30 Gew.-Teile eines feinteiligen hydrophoben teilchenförmigen Materials (B) und 0 bis 20 Gew.-Teile eines Organosiliciumharzes (C), das im wesentlichen aus Triorganosiloxangruppen und $SiO_{4/2}$ -Gruppen besteht, umfaßt.

2. Schaumsteuerungsmittel nach Anspruch 1, dadurch gekennzeichnet, daß die Organopolysiloxane Polydiorganosiloxane der folgenden allgemeinen Struktur sind:



worin R und R'' die oben angegebene Bedeutung besitzen, R^o entweder für eine Gruppe R oder für eine Gruppe R' steht, b und c die oben angegebene Bedeutung besitzen und x und y jeweils unabhängig voneinander für eine ganze Zahl stehen.

3. Schaumsteuerungsmittel nach Anspruch 2, dadurch gekennzeichnet, daß die gesamte Kettenlänge (x+y+2) 40 bis 500 Siloxaneinheiten umfaßt.

4. Schaumsteuerungsmittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Gruppen R' eine Kohlenstoffkette von 10 bis 24 Kohlenstoffatomen aufweisen.

5. Schaumsteuerungsmittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Komponente (B) Siliciumdioxid mit einer mittleren Teilchengröße von 0,1 bis 50 µm und einer Oberfläche von mindestens 50 m²/g ist, wobei die Oberfläche hydrophob gemacht wurde.

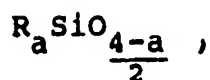
6. Schaumsteuerungsmittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Komponente (C) in einer Menge von 5 bis 10 Gew.-Teilen vorhanden ist.

7. Schaumsteuerungsmittel nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es in Form einer Emulsion oder Dispersion vorliegt.

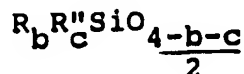
8. Detergensenzusammensetzung in Pulverform, die eine Detergensenkomponente und ein Schaumsteuerungsmittel umfaßt, dadurch gekennzeichnet, daß das Schaumsteuerungsmittel ein solches gemäß einem der vorhergehenden Ansprüche ist.

9. Detergensenzusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß das Schaumsteuerungsmittel in einer Menge von 0,02 bis 25 Gew.-%, bezogen auf die gesamte Detergensenzusammensetzung, vorhanden ist.

10. Verfahren zur Steuerung des Schäumens einer wäßrigen Lösung eines grenzflächenaktiven Mittels in einer Umgebung mit freier Oberflächendurchwirbelung durch Vermischen der Lösung mit 5×10^{-4} bis 10 Gew.-% der grenzflächenaktiven Lösung eines Schaumsteuerungsmittels, das dadurch gekennzeichnet ist, daß es (A) 70 bis 99,9 Gew.-Teile eines Organopolysiloxans, dessen Siloxaneinheiten im wesentlichen aus 0-60% Einheiten der allgemeinen Formel (i)



5 worin R für eine Kohlenwasserstoffgruppe mit bis zu 8 Kohlenstoffatomen steht und a einen Wert von 0 bis 3 besitzt, und aus 40-100% Einheiten der allgemeinen Formel (ii)



10 bestehen, worin R'' für eine Gruppe -Z_z-R' steht, worin R' für eine Alkylgruppe mit 9 bis 35 Kohlenstoffatomen steht, Z für eine Verbindungsgruppe zwischen Silicium und R' steht und z einen Wert von 0 oder 1 besitzt, b einen Wert von 0, 1 oder 2 besitzt, c einen Wert von 1 oder 2 besitzt und b+c einen Wert von 1, 2 oder 3 besitzt, wobei gilt, daß
15 mehr als 70 Gew.-% des Kohlenstoffgehalts des Organopolysiloxans auf die Gruppen R'' zurückzuführen ist,

(B) 0,1 bis 30 Gew.-Teile eines feinteiligen hydrophoben teilchenförmigen Materials und (C) 0 bis 20 Gew.-Teile eines Organosiliciumharzes, das im wesentlichen aus Triorganosiloxangruppen und SiO_{4/2}-Gruppen besteht,
20 umfaßt.

Revendications

1. Un agent inhibiteur de mousse qui est exempt d'huiles hydrocarbonées et comprend un organopolysiloxane (A),
25 une matière particulaire hydrophobe finement divisée (B) et facultativement une résine organosiliciée (C), caractérisé en ce qu'il comprend 70 à 99,9 parties en poids d'organopolysiloxane (A) dont les motifs siloxanes consistent essentiellement en 0 à 60 % de motifs de la formule générale (i) R_aSiO_{(4-a)/2} où R représente un groupe hydrocarboné ayant au plus 8 atomes de carbone et la valeur de a est de 0 à 3, et en 40 à 100 % de motifs de la formule générale (ii) R_bR'_cSiO_{(4-b-c)/2} où R'' représente un groupe -Z_z-R' où R' représente un groupe alkyle ayant 9 à 35
30 atomes de carbone, Z représente un groupe de liaison entre le silicium et R' et la valeur de z est 0 ou 1, la valeur de b est 0, 1 ou 2, la valeur de c est 1 ou 2, et la valeur de b+c est 1, 2 ou 3, à condition que les groupes R'' contribuent pour plus de 70 % en poids à la teneur en carbone de l'organopolysiloxane, 0,1 à 30 parties en poids d'une matière particulaire hydrophobe finement divisée (B) et 0 à 20 parties en poids d'une résine organosiliciée (C) constituée essentiellement de groupes triorganosiloxanes et de groupes SiO_{4/2}.

2. Un agent inhibiteur de mousse selon la revendication 1, caractérisé en ce que les organopolysiloxanes sont des polydiorganosiloxanes ayant la structure générale
R'_c R_bSi-O-[R''Si-O]_x-[R₂Si-O]_y-SiR_bR'_c
où R et R'' sont tels que définis ci-dessus, R° représente un groupe R ou un groupe R'', b et c sont tels que définis
40 ci-dessus, et x et y représentent chacun indépendamment un nombre entier.

3. Un agent inhibiteur de mousse selon la revendication 2, caractérisé en ce que la longueur de chaîne totale (x+y+2) comprend 40 à 500 motifs siloxanes.

4. Un agent inhibiteur de mousse selon l'une quelconque des revendications précédentes, caractérisé en ce que les groupes R' ont une chaîne carbonée de 10 à 24 atomes.

5. Un agent inhibiteur de mousse selon l'une quelconque des revendications précédentes, caractérisé en ce que le Composant (B) est de la silice ayant une taille moyenne de particules de 0,1 à 50 µm et une surface d'au moins 50
50 m²/g, ladite surface ayant été rendue hydrophobe.

6. Un agent inhibiteur de mousse selon l'une quelconque des revendications précédentes, caractérisé en ce que le Composant (C) est présent en une quantité de 5 à 10 parties en poids.

7. Un agent inhibiteur de mousse selon l'une quelconque des revendications précédentes, caractérisé en ce qu'il est fourni sous la forme d'une émulsion ou d'une dispersion.

8. Une composition détergente sous forme de poudre comprenant un composant détergent et un agent inhibiteur de

mousse, caractérisée en ce que l'agent inhibiteur de mousse est conforme à l'une quelconque des revendications précédentes.

9. Une composition détergente selon la revendication 8, caractérisée en ce que l'agent inhibiteur de mousse est présent en une quantité de 0,02 à 25 % en poids par rapport à la composition détergente totale.
10. Un procédé de lutte contre la mousse d'une solution aqueuse d'agent tensio-actif dans un environnement engendrant une turbulence de surface libre, qui consiste à mélanger ladite solution avec 5×10^{-4} à 10 % en poids, par rapport au poids de la solution d'agent tensio-actif, d'un agent inhibiteur de mousse, caractérisé en ce que l'agent inhibiteur de mousse comprend (A) 70 à 99,9 parties en poids d'un organopolysiloxane dont les motifs siloxanes consistent essentiellement en 0 à 60 % de motifs de la formule générale (i) $R_aSiO_{(4-a)/2}$ où R représente un groupe hydrocarboné ayant au plus 8 atomes de carbone et la valeur de a est de 0 à 3, et en 40 à 100 % de motifs de la formule générale (ii) $R_bR'_cSiO_{(4-b-c)/2}$ où R'' représente un groupe $-Z-Z'$ où R' représente un groupe alkyle ayant 9 à 35 atomes de carbone, Z représente un groupe de liaison entre le silicium et R' et la valeur de z est 0 ou 1, la valeur de b est 0, 1 ou 2, la valeur de c est 1 ou 2, et la valeur de $b+c$ est 1, 2 ou 3, à condition que les groupes R'' contribuent pour plus de 70 % en poids à la teneur en carbone de l'organopolysiloxane, (B) 0,1 à 30 parties en poids d'une matière particulaire hydrophobe finement divisée et (C) 0 à 20 parties en poids d'une résine organosiliciée constituée essentiellement de groupes triorganosiloxanes et de groupes $SiO_{4/2}$.

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